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Research Article

The Synthesis of Melamine Cored Schiff Bases and Investigation of Heteronuclear Metal Complexes

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ABSTRACT

In this study, 2,4,6-triamino-s-triazine (melamine) is the starting material. The condensation reaction of melamine and 4-hydroxybenzaldehyde resulted in the formation of the monopodal Schiff base. An oxygen-bridged monopodal complex of [(Fe(III)Salophen)Cl] ligand complex with monopodal Schiff base ligand was then obtained. Tripodal Schiff base ligand was obtained by condensing 2-hydroxybenzaldehyde with a monopodal complex and this ligand in some transition metal complexes were synthesized. As a result, the ligand and complexes of this ligand were isolated, as well as elemental analyses, FT-IR, ^{1}H-NMR, TGA and magnetic susceptibility measurements of the obtained compounds were taken to elucidate their structures.

Araştırma Makalesi

Melamin Merkezli Schiff Bazlarının Sentezi ve Heteronükleer Metal Komplekslerinin İncelenmesi

MAKALE BİLGİSİ

Makale Geçmişi
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Schiff baz
Melamin
Salophen

ÖZ

Bu çalışmada başlangıç materyali olarak 2,4,6-triamino-s-triazin (melamin) kullanıldı. Melamin ve 4-hidroksibenzaldehitin kondenzayon reaksiyonu monopodal Schiff bazının oluşmasıyla sonuçlandı. Daha sonra monopodal Schiff bazı ligandı ile [(Fe(III)Salophen)Cl] ligand kompleksi bir oksijen köprülü monopodal kompleks elde edildi. Monopodal kompleks ile 2-hidroksibenzaldehitin kondenzayonu ile tripodal Schiff baz ligandı elde edilerek bu ligandın bazı geçiş metal kompleksleri sentezlendi. Sonuç olarak, ligandı ve bu ligandın kompleksleri izole edildi, ayrıca elde edilen bileşiklerin elementel analizleri, FT-IR, ^{1}H-NMR, TGA ve manyetik süsebtibilite ölçümleri alınarak yapıları aydınlatıldı.

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Bu çalışmanın hazırlanma sürecinde bilimsel ve etik ilkelere uyulduğu ve yararlanılan tüm çalışmaların kaynakçada belirtildiği beyan olunur (Z.E. Koç). It is declared that scientific and ethical principles have been followed while carrying out and writing this study and that all the sources used have been properly cited (Z.E. Koç).
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Yazar, bu makalede bildirilen çalışmayı etkiliyor gibi görünebilecek bilinen hiçbir rakip mali çıkarları veya kişisel ilişkileri olmadığını beyan eder. The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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1. Introduction

Melamine is an organic compound that functions as a base and comprises three cyanamide molecules. (Hazra et al., 2014). Melamine, with its 1,3,5-triazine structure, is a significant industrial substance widely utilized as a flame retardant in polymer engineering and as a fertilizer in agriculture. It is also employed in the manufacturing of plastic materials (Horacek and Pieh, 2000). Thermosetting plastic (Panyakapo and Panyakapo, 2008), Formica (Fodey et al., 2011), laminate flooring and dry erase boards (Uysal and Koç, 2010). In addition, melamine foams, polymers derived from melamine, serve as effective insulation and soundproofing materials. They are also used in the production of polymeric cleaning products like Magic Eraser. (Wang and Zhang, 2004; Uysal, 2013; Uysal and Koç, 2016). Heterocyclic compounds are increasing in use in polymer, coordination chemistry, environmental, biochemistry, dyestuff and pharmaceutical (Wimmer et al., 1992; Uysal et al., 2012). Furthermore, s-triazine Schiff base compounds are used in medicine, especially as molecular magnetic materials, and such heterocyclic compounds are used as active ingredients of antitumor and anticancer drugs (Koc and Uysal, 2016; Arslaner et al., 2017; Ozer et al., 2023).

s-Triazine compounds have gained importance in environmental chemistry, metal-organic lattice structures and gas storage (Yu et al., 2008). 2,4,6-Triamino-s-triazine was used as the core s-triazine group in the synthesis of Schiff base ligands (Uysal and Koc, 2016). Since melamine has symmetrical three-way amine groups, Schiff base-containing 2,4,6-triamino-s-triazine ligands were obtained by condensation reaction with different aldehyde groups (Koc and Uysal, 2016). Multipodal melamine-cored ligands heteronuclear complexes were obtained by coordinating the melamine with the salophen ligand complexes with a single oxygen (Celikbilek and Koc, 2014). s-Triazine [(Fe(III)/Salophen)] and transition metal complexes were obtained by these complexes with aldehydes (Karipcin and Karatas, 2001; Uysal, 2013).

2. Experimental

2.1. Materials

Elemental analyses were performed using a Leco, CHNS-932 model analyzer. ^{1}H NMR spectra were recorded by the Varian, 400 M spectrometer. FT-IR spectra were recorded using a Perkin-Elmer Spectrum 100 with Universal ATR Polarization Accessory. Magnetic susceptibilities of the metal samples were measured at 296 K using a Sherwood Scientific MX Gouy magnetic susceptibility apparatus with $Hg[Co(SCN)_4]$ as a calibration by the constant magnetic field.

2.2. 4-((4,6-diamino-1,3,5-triazine-2-imino) methyl) phenol [MHBA]

Synthesis of [MHBA] was synthesized according to the cited literature (N. Yıldırım, 2023), (Figure 1).

2.3. Synthesis of salophen ligand and complexes

Synthesis of salophen ligands and salophen complexes were synthesized according to the cited literature. (Kopel et al., 1998; Gembicky et al., 2000), (Figure 2).

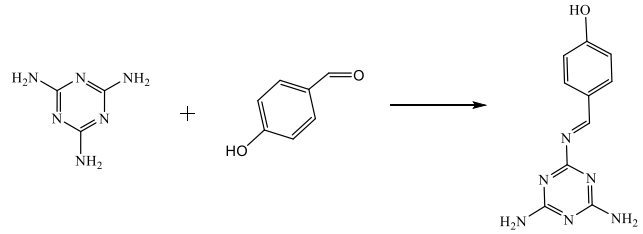

Figure 1. Monopodal Schiff base ligand [MHBA].

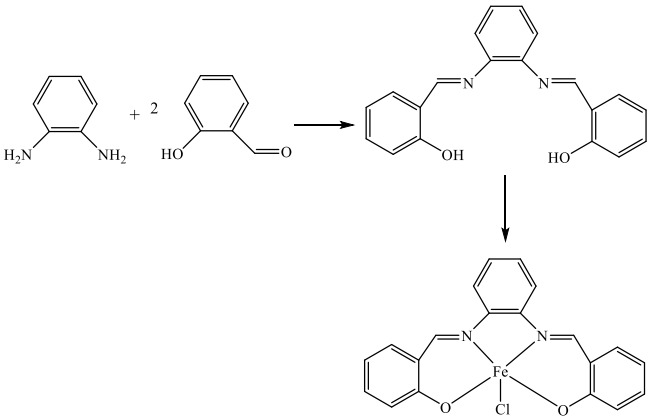

Figure 2. Salophen ligand and [Fe(salophen)Cl] complex.

2.4. Synthesis of 4-((4,6-diamino-1,3,5-triazine-2-imino)methyl)phenol [MHBAFe(III)(salophen)] complex

Synthesis of [MHBAFe(III)(salophen)] was synthesized according to the cited literature (N. Yıldırım, 2023), (Figure 3).

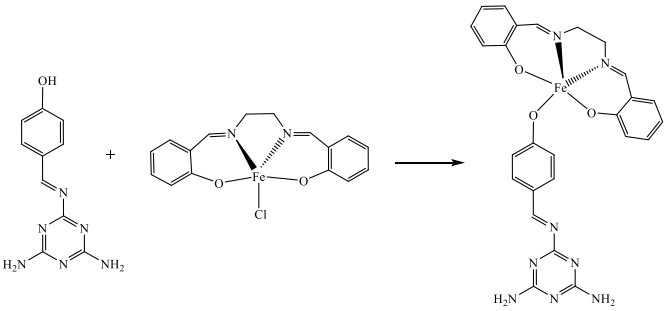

Figure 3. Monopodal Schiff base ligand [MHBAFe(III)(salophen)] complex.

2.5. Synthesis of 2,2'-(6-(((4-hydroxybenzylidene)amino)-1,3,5-triazine-2,4 diyl) bis (azanylylidene)) bis (methanylylidene))diphenol [SALMHBAFe(III)(salophen)]

[MHBAFe(III)(salophen)] (1 mmol, 0.57 g,) was dissolved in 30 mL of methanol and stirred under reflux for one hour. 2-Hydroxybenzaldehyde (2 mmol, 0.25 mL) 20 mL methanol was added to the resulting mixture. The mixture was reflux for 4 h and 5 drops of acetic acid catalyst was added. It was mixed for a while until the powder formed and a color change was observed. The precipitate was filtered. [SALMHBAFe(III)(salophen)]: FT-IR (cm^{-1}) 3340, 3123 (OH), 1653,1631 (C=N), 1547 ($C=N_{triazine}$), (Figure 4).

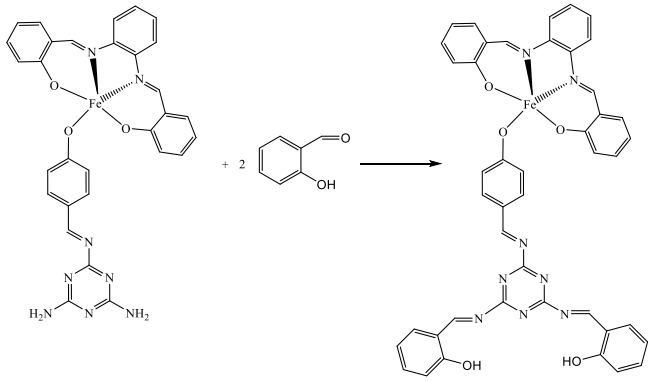

Figure 4. Tripodal Schiff base ligand [SALMHBAFe(III)(salophen)] complex.

2.6. Synthesis of 2,2'-(6-(((4-hydroxybenzylidene)amino)-1,3,5-triazine-2,4-diyl) bis (azanylylidene)) bis (methanylylidene)) diphenol [MSALMHBAFe(III)(salophen)] heteronuclear complexes (M=Co(II), Ni(II), Cu(II))

Suspension of [MSALMHBAFe(III)(salophen)] heteronuclear complexes (1 mmol 0.85 g.) in 20 mL of ethanol was prepared in a 100 mL flask on 1 mmol ($Co(CH_3COO)_2.4H_2O$ (0.25 g.), $Cu(CH_3COO)_2.H_2O$ (0.20 g.), $Ni(CH_3COO)_2.4H_2O$ (0.25 g.)) were added in 20 mL ethanol. Boiled under a back cooler for 3 h. at around 80 ^oC. The solvent was evaporated by half and allowed to cool (under room conditions). Then, half of the water was added, left for a day, filtered in a vacuum, washed with water and dried in an oven at 105 ^oC. [Co(II)SALMHBAFe(III)(salophen)]: FT-IR (cm^{-1}) 1676,1624, (C=N), 1535 ($C=N_{triazine}$). [Ni(II)SALMHBAFe(III)(salophen)]: FT-IR (cm^{-1}) 1675,1629 (C=N), 1534 ($C=N_{triazine}$). [Cu(II)SALMHBAFe(III)(salophen)]: FT-IR (cm^{-1}) 1683, 1624 (C=N), 1539 ($C=N_{triazine}$), (Figure 5).

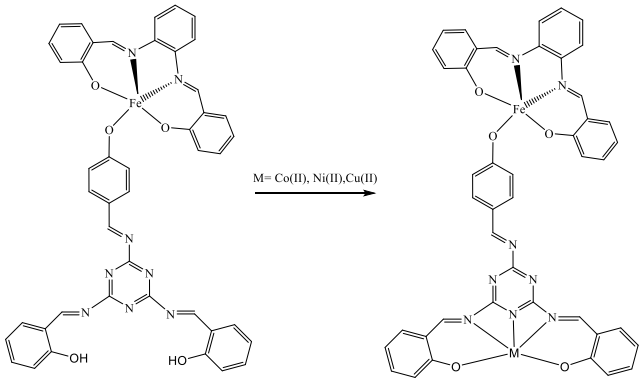

Figure 5. Tripodal Schiff base ligand [MSALMHBAFe(III)(salophen)] heteronuclear complex.

3. Results and Discussion

In this study, Melamine and 2-hydroxybenzaldehyde were used as starting material and s-triazine Schiff base monomer [MHBA] was synthesized. Single oxygen coordinated bridged monomer complex structures obtained [MHBAFe(III)(salophen)] with synthesized [MHBA] and [Fe(III)(salophen)Cl] complexes are 2-hydroxybenzaldehyde (Salicylaldehyde) Schiff base complexes [SALMHBAFe(III)(salophen)] were obtained. Two oxygen and tri nitrogen coordinated bridged complex structures obtained [MSALMHBAFe(III)(salophen)] with [Fe(III)salophenMHBASAL] and ($Co(CH_3COO)_2.4H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2.H_2O$ heteronuclear complexes were obtained.

When OH protons were examined in the ^1H NMR spectrum of the [MHBA] ligand, a singlet chemical shift corresponding to OH protons occurred at 9.76 ppm. In addition, two doublet chemical shift values of the aromatic ring were observed at 7.74-7.72 ppm, 6.89-6.91 ppm and CH=N singlet chemical shift values at 8.39 ppm. (Figure 6) (Tahmassebi and Sasaki, 1998).

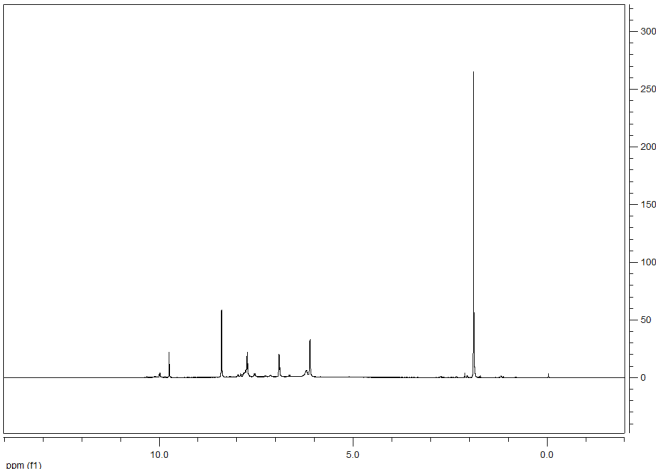

Figure 6. ^1H NMR Spectrum of [MHBA].

The OH peaks of the [MHBA] ligand were observed as 3324 cm^{-1} and the CH=N Schiff base group was observed as a stretching vibration of 1649 cm^{-1}. In addition, it has been observed that OH peaks disappear in the monopodal complex of the [MHBA] ligand as a result of coordination with the [Fe(III)(salophen)Cl] synthesized from the literature with a single oxygen (Figure 7-8). (Figure 9-10) (Koc and Ucan, 2007; N. Yıldırım, 2023).

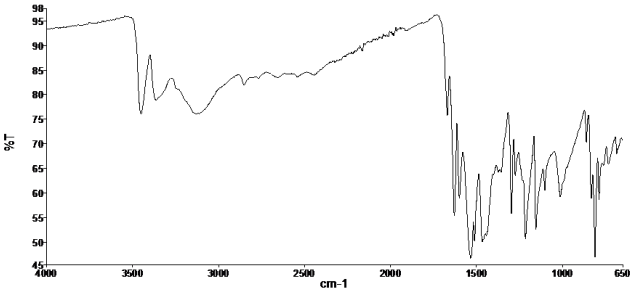

Figure 7. FT-IR spectrum of [MHBA].

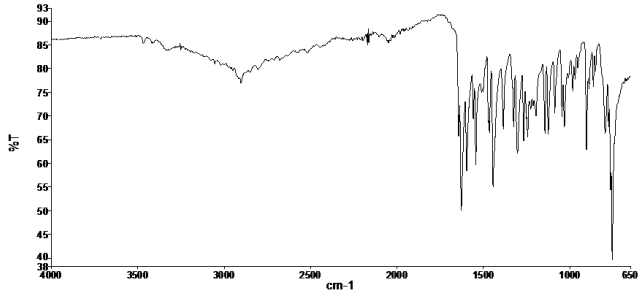

Figure 8. FT-IR spectrum of [MHBAFe(III)(salophen)].

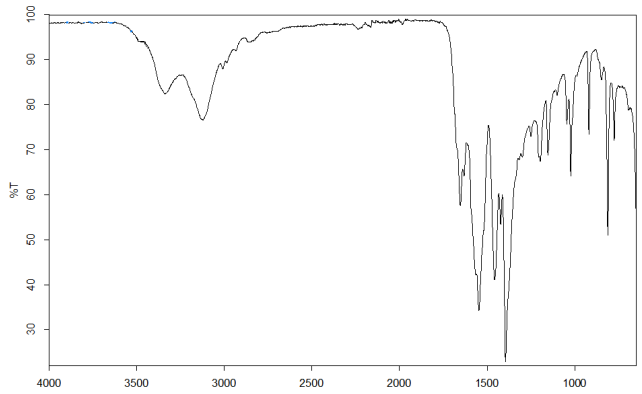

Figure 9. FT-IR spectrum of [SALMHBAFe(III)(salophen)].

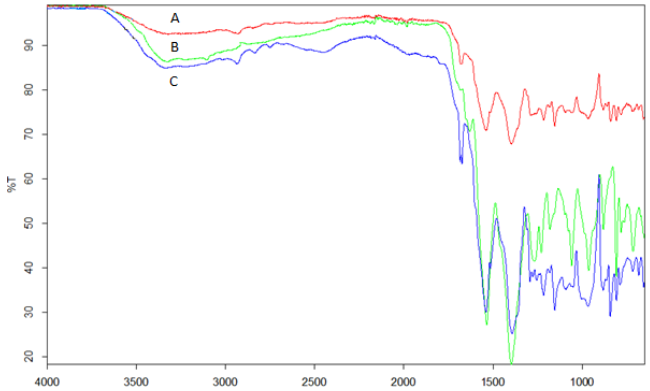

Figure 10. FT-IR spectrum of [MSALMHBAFe(III)(salophen)] (A: Co(II), B: Ni(II), C: Cu(II)).

Synthesized [MHBA] and [(Fe(III)salophen)Cl], complexes [MHBAFe(III)(salophen)] were obtained with weak field effect for the BM values of 5.27, and $t_{2g}^3eg^2$ were observed, respectively. As a result, it was estimated to have a triangular pyramidal (dsp^3) geometric structure, since it showed a weak field complex feature. As a result, since the complex structures have the d^5 electron configurations calculated theoretically, (Table 1) (Koc and Ucan, 2008; N. Yıldırım, 2023). Then, heteronuclear complex structures were obtained with the ligand complex [Co(II)/Ni(II)/Cu(II)] of the ligand [MSALMHBAFe(III)(salophen)]. The theoretical BM values expected in heteronuclear structures of the [MHBAFe(III)(salophen)] ligand complex yield lower BM values than expected values with Co(II) d^7 ($t_{2g}^5e_g^2$), Ni(II) d^8 ($t_{2g}^6e_g^2$), Cu(II) d^9 ($t_{2g}^6e_g^3$), metal ion arrangement of 1.73 BM corresponding to a single electron and Co(II) 1.65, Cu(II) 1.67 and Ni(II) diamagnetic BM values, respectively It has been associated with antiferromagnetic action. Looking at these structures, we think that geometry is a square pyramid and hybridization is dsp^3.

TGA measurement of [MHBAFe(III)(salophen)] was made. According to the TGA diagram of gaseous H_2O, CO_2, C_6H_6, N_2 and H_2 are first removed from the environment and at 155, 325 and 455 °C 64.32% (Theoretical: 65.46%) three-step It is observed that the decomposition reaction that takes place is a total mass loss. However, at 800-880 °C, the mass loss of matter continues. It is estimated that this is due to the presence of the triazine ring and metal oxides in the environment (Figure 11) (Karipcin and Karatas, 2001).

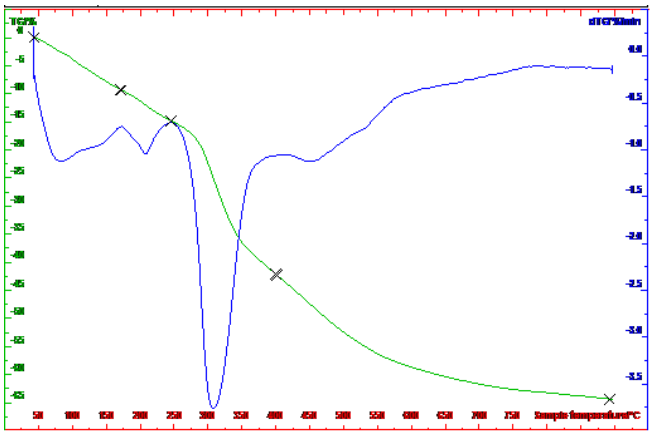

Figure 11. TGA spectrum of [MHBAFe(III)(salophen)]

Table 1. Physical properties of ligands and complexes.

Compounds	Color	Yield (%)	M.P. (°C)	μ_{eff}	Found (Calculated) (%)		
					C	H	N
$C_{10}H_{10}N_6O$ [MHBA]	White	80	183	-	53.17 (52.17)	4.75 (4.38)	36.48 (36.50)
$C_{27}H_{26}FeN_8O_3$ [MHBAFe(III)(salophen)]	Black	75	160	5.27	57.09 (57.26)	4.98 (4.63)	19.83 (19.72)
$C_{45}H_{34}FeN_8O_5$ [SALMHBAFe(III)(salophen]	Orange	80	290	5.36	65.75 (65.70)	4.12 (4.17)	13.65 (13.62)
$C_{45}H_{32}CoFeN_8O_5$ [Co(II)SALMHBAsalophenFe(III)]	Yellow	70	300*	3.44	61.47 (61.45)	3.66 (3.67)	12.78 (12.74)
$C_{45}H_{32}NiFeN_8O_5$ [Ni(II)SALMHBAsalophenFe(III)]	Green	65	300*	4.83	61.40 (61.47)	3.59 (3.67)	12.76 (12.74)
$C_{45}H_{32}CuFeN_8O_5$ [Cu(II)SALMHBAsalophenFe(III)]	Brown	60	300*	3.57	61.15 (61.13)	4.60 (3.65)	12.64 (12.67)

*Decomposition

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